NASA-CR-197995

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Bauer

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Dr. Michael Bicay
Infrared and Radio Branch
Astrophysics Division, EZ (GSL)
NASA
Washington, D. C. 20546

ReL Grant # NAGW-1262

Dear Dr. Bicay:

I have endclosed, for your files, three copies of my final report covering the portion of our project that covers studies of infrared emissions from heated simple hydrocarbons. As noted, we are continuing with investigations of nucleation/condensation of supersaturated metal vapors.

I plan to convert the material covered in this report for publication in Astronomi9cal Astrophysics.

Do you wish to receive additional copies of this report?

*Was published in Spectrochim Acta 50A

Sincerely,

Simon H. Bauer
Professor of Physical Chemistry

SHB:jp
Enc.

(NASA-CR-197995) FINAL TECHNICAL REPORT (Cornell Univ.) 8 p

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PART II. SUMMARY OF COMPLETED PROJECT

This project consisted of two components: (i) interpretation of emission spectra (in the infrared) as recorded from various astronomical sources, and (ii) determination of combinations of pressure and temperature that lead to the condensation of metals, metal oxides, metal silicides, under supersaturated conditions, to mimic the generation of interstellar grains. We undertook experiments in two types of shock-tubes designed to address the above questions. Also, we continued with the development of our kinetic-molecular-model for calculating condensation fluxes.

Regarding (i): we demonstrated (report completed) that when selected low molecular weight hydrocarbons (alkyl substituted dienes) are heated to $\propto 1500^{\circ}$K, their emission spectra in the 3.3 μm region match closely the reported IR bands. Furthermore,using their absorption spectra as a guide we concluded that overall (3.3 - 11.3 μm), hot low molecular weight hydrocarbons of this class comprise a more likely source of the reported astronomical emissions than do the calculated spectra of poly-aromatic-hydrocarbons, as currently postulated.

Regarding (ii): One of our old shock tubes was converted for shock initiation by opening a rapidly acting valve (~5 ms). While it has taken longer than we anticipated to bring this unit into full operation, the resulting apparatus is unique in several repects. Shock speed reproducibility is as good as our ability to record time intervals (± 0.2 μs out of 500 μs); all operations are electrically controlled; no diphragm debris is generated, so that the shock-tube need not be opened between runs, thus preventing atmospheric contaminations; turn-around times are approximately 10 min; the laser-schlieren diagnostic is very sensitive for measuring energy transfers between the reacting species --- indeed, we have not yet reached its noise limit. Concurrently, shock-tube computer codes were developed to calculate density-gradient functions for any specified combination of endo-exo-ergic steps, to match postulated with observed scans. Our kinetic-molecular model for computing the dependence of condensation fluxes on temperature and levels of supersaturation was expanded, and applied to a large variety of systems for which data are in the literature.

PART III. TECHNICAL INFORMATION

A compact summary of accomplishments supported by this program is the compilation of five abstracts that summarize the content of manuscripts wherein experimental and computational results are presented in detail.

[In: Proceedings of International Symposium on Shock Waves and Tubes. Ed. Y.M. Kim, API, New York (1990), p.600]

TIME RESOLVED SPECTRA IN THE INFRARED --- ABSORPTION AND EMISSION FROM SHOCK HEATED HYDROCARBONS

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ABSTRACT

We have extended the wavelength range of our previously constructed multichannel, fast recording spectrometer to the mid-infrared. With the initial configuration, using a silicon-diode (photovoltaic) array, we recorded light intensities simultaneously at 20 adjacent wavelengths, each with 20 μs time resolution. For studies in the infrared the silicon diodes are replaced by a 20 element PbSe (photoconducting) array of similar dimensions (1×4 mm/element), cooled by a three-stage thermoelectric device. These elements have useful sensitivities over 1.0-6.7 μm. Three interchangeable gratings in a 1/4 m monochromator cover the following spectral ranges: 1.0-2.5 μm (resolution 33.6 cm^{-1}); 2.5-4.5 μm (16.8 cm^{-1}); 4.0-6.5 μm (16.7 cm^{-1}). Incorporated in the new housing there are individually controlled bias-power sources for each detector, two stages of analogue amplification and a 20-line parallel output to the previously constructed digitizer, and record/hold computer.

The immediate application of this system is the study of emission and absorption spectra of shock heated hydrocarbons --- C_2H_2, C_4H_4 and C_6H_6 --- which are possible precursors of species that generate infrared emissions in the interstellar medium. It has been recently proposed that these radiations are due to PAH that emit in the infrared upon relaxation from highly excited states. However, it is possible that such emissions could be due to shock-heated low molecular-weight hydrocarbons, which are known to be present in significant abundances, ejected into the interstellar medium during stellar outer atmospheric eruptions.

The full Swan band system appeared in time-integrated emission spectra from shock heated C_2H_2 (1% in Ar; T_{5eq} = 2500K); no soot was generated. At low resolution the profiles on the high frequency side of the black body maximum show no distinctive features. These could be fitted to Planck curves, with temperatures that declined with time from an initial high that was intermediate between T_5 (no conversion) and T_5(eq).

ACKNOWLEDGMENTS

This study is supported jointly by the Astrophysics Section of the National Science Foundation (AST-8704623) and by the corresponding section of NASA (NAGW-1262). C. R. Dunnam designed and constructed the new PbSe electronics unit.

[In: Journal of Chemical Physics, 94, 8302 (1991)]

ESTIMATION OF HOMOGENEOUS NUCLEATION FLUX VIA A KINETIC MODEL

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ABSTRACT

The proposed kinetic model for condensation under homogeneous conditions, and the onset of unidirectional cluster growth in supersaturated gases, does not suffer from the conceptual flaws that characterize classical nucleation theory. When a full set of simultaneous rate equations is solved a characteristic time emerges, τ_n, for each cluster size, at which the production rate, and its rate of conversion to the next size (n+1) are equal. Procedures for estimating the essential parameters are proposed; condensation fluxes J^{ss}_{kin}, are evaluated. Since there are practical limits to the cluster size that can be incorporated in the set of simultaneous 1st order differential equations, a code was developed for computing an approximate J^{ss}_{th}, based on estimates of a "constrained equilibrium" distribution, N^{eq}_{u}, and identification of its minimum, N^{eq}_{ℓ}.

ACKNOWLEDGMENTS

This computational analysis was supported in part by NASA grant NAGW-1252 and NSF grant AST-8704623. We hereby express our thanks. We also thank Professors Katz and Schmitt for sending us copies of their data tables.

[Accepted for publication: Journal of Physical Chemistry, Jan. 1993]

Condensation Flux Estimates Derived *via* a Kinetic-Molecular Model

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ABSTRACT

The readily calculable format of our previously published kinetic-molecular model for condensation rates was tested on fourteen diverse systems. A single adjustable parameter (SP) that represents the collisional efficiency for removal of the heat of condensation (and thus stabilizes the nascent clusters), permits estimation of flux values to well within the experimental error limits. The deduced range of excursions of SP is 0.2 to 1.0; it increases with declining temperature. This trend parallels the temperature dependence observed for other direct association reactions and for de-excitation cross-sections of energized molecules undergoing unimolecular dissociations. Regrettably, there are no reliable data for condensation rates from supersaturated vapors of metals, metal oxides or other refractory materials upon which our model can be tested.

ACKNOWLEDGMENT

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[Submitted for publication: Review of Scientific Instruments]

A PISTON ACTUATED SHOCK-TUBE, WITH LASER-SCHLIEREN DIAGNOSTICS

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ABSTRACT

We describe the essential construction features of a piston actuated shock tube, and list its advantages relative to the conventional use of diaphragm ruptures for shock initiation. Typical operational parameters are presented to illustrate the levels of reproducibility we achieved. The application of this tube for recording post shock front density gradients *via* the laser-schlieren technique is described.

ACKNOWLEDGMENT

This work was supported in part by grants from NSF (Division of Astronomical Sciences: AST-8704623) and NASA (Astrophysics Division: NAGW-1262). Our appreciation is hereby noted.

[In preparation: to be submitted to --- Astronomy and Astrophysics]

INFRARED EMISSIONS FROM SHOCK HEATED HYDROCARBONS

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ABSTRACT

The objective of this project was to ascertain whether low molecular weight hydrocarbons [LMHC] in the range of C_2 to C_6, upon heating to temperatures above 1000°K, emit infrared radiations at frequencies that correspond to the "unidentified infrared" (UIR) features --- the recorded emissions from a variety of astronomical sources --- reflection nebulae, HII regions, planetary nebulae, spiral galaxies and other extra galactic objects. In this report we: (i) briefly review the principal hypotheses proposed for the origin of UIR bands and call attention to the fact that none is completely consistent with the observed spectra; (ii) suggest that the arguments presented against emissions from LMHC species as possible sources are not valid; (iii) describe the IR emission spectra recorded from shock-heated gases [C_2H_2; $(H_3C)_2C{=}CH_2$; $H_2C{=}C(CH_3){-}C(CH_3){=}CH_2$; $(H_3C)_2C{=}C(H){-}C(CH_3){=}CH_2$] due to excitation of the fundamental C-H stretching vibrations; and (iv) briefly account for the observed times dependent IR band profiles from the hot hydrocarbons. While the infrared emission anticipated over the entire spectral range from LMHC do not provide a perfect match to UIR, the correspondences, in several respects, are better than the emissions anticipated from PAH species.